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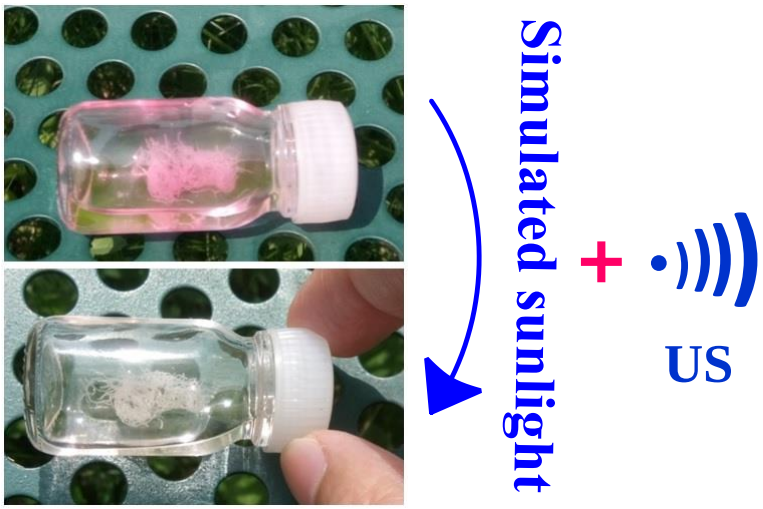
The Authors declare no conflict of interest.

GRAPHICAL ABSTRACT



ABSTRACT

The effect of sonication on the photodegradation of Rhodamine 6G (Rh6G, a fluorone dye) using woven cotton fabrics decorated with TiO_2 nanoparticles (NPs) has been investigated. TiO_2 NPs were synthesized in situ by sol-gel method in the presence of cotton textile and then hydrothermally treated. TiO_2-loaded fabrics were treated ultrasonically to test adhesion to- and properties of the NPs on the fabrics. We demonstrate good adhesion and a good stability of the NPs of TiO_2. Moreover, sonication substantially improved the distribution on the surfaces and hence enhanced the fabrics catalytic activity. Either under UV or simulated sunlight, ultrasonicated fabrics were found to have a high photocatalytic activity towards Rh6G, used as a model dye. SEM, XPS, UV-Vis and FTIR spectroscopy, as well as ground state diffuse reflectance (GSDR) and laser induced luminescence (LIL) were used to characterize fabrics/TiO_2 samples in terms of topography, surface composition, influence of hydrothermal treatment on photocatalytic activity, stability of TiO_2 NPs, electro-optical properties of the modified fabrics, as well as the effect of ultrasonication on the photodegradation of Rh6G. This work paves the way to a larger scale improvement of the photocatalytic performances of TiO_2-loaded cotton fabrics by post-sonication.

Keywords: cotton fabrics, TiO_2 nanoparticles, adhesion, sonication, Rhodamine 6G, photodegradation of dyes.

Introduction

Currently, there is a growing demand for imparting textiles a technical property in addition to their intrinsic function of clothing. Indeed, functionalized textiles **(Horrocks and Anand 2000; Blaser et al. 2008**), are used for different applications such as comfort (odour elimination) (**Yuranova et al. 2006; Chen et al. 2010**), biomedical (prostheses, implants, bandages ...) (**Li et al. 2015**), civil engineering (composites, geotextile...) (**Fangueiro 2011**) and protection of individuals (protective clothing (**Scott 2005**), clothes for military **(Wilusz 2008**) or firemen (**Hristian et al. 2014**). Protection can also be provided for public ready-to-wear clothes using textiles with protective TiO_2 nanoparticles. These nanomaterials protect the skin from the UV-B (290-320 nm) and UV-A (320-400 nm) regions of the solar spectrum (**Popov et al. 2005**), which consists of three ranges: UV-A, UV-B and UV-C (**McKinlay 1987; Diffey 1991)** (100 to 290 nm) being almost completely absorbed by the ozone layer in the upper part of the Earth atmosphere.

To these above-mentioned remarkable features, one can also design textiles that possess photocatalytic properties imparted by immobilized TiO_2 nanoparticles **(Bozzi et al. 2005; Meilert et al. 2005; Xue et al. 2008; Abidi et al. 2009; Abid et al. 2016**) for the elimination of dyes, fats, bacteria and viruses (**Bozzi et al. 2005**). It is well-known that titanium dioxide in its crystalline anatase form is considered as the semiconductor oxide having the highest photocatalytic activity and the best quantum yield (reaction rate in moles per second) (**Hadjiivanov and Klissurski 1996**).The photocatalytic activity of TiO_2 rests on its excitation with light the energy of which $h\nu \geq Eg$ (band gap energy) to create an electron pair (e^-)/hole (h^+) by the transfer of an electron of the valence band to the conduction band. This electron can be ejected and will react with oxygen adsorbed on the surface of TiO_2, while the hole h^+ created can react with surface water, forming highly oxidizing hydroxyl radicals (OH°) responsible for the degradation of pollutants (**Min et al. 2007; Salvador 2007; Tariq et al. 2008; Ochiai and Fujishima 2012)**. In addition to these salient chemical reactivity features, TiO_2 is industrially employed due to its chemical stability, non-toxicity and low cost.

Either dyes or pigments employed in the textile industry undergo numerous testing; probably the most important one is colour fastness (**Mohammad 2015; Rehman et al. 2017**). It is thus important to investigate the adhesion of TiO_2 NPs to cotton textile in order to understand the shelf life of the textile and its long-term use to catalyse the degradation of dyes. Dealing with technical textile loaded with TiO_2 immobilized for photocatalytic purpose,

we have envisioned testing the stability of the immobilized nanocatalysts in terms of their (i) adhesion, and (ii) photoactivity. In an academic laboratory scale, ultrasonication remains a simple procedure to test the shaking off of the nanoparticles away from the textile support. However, it was also necessary to investigate the reminiscent photoactivity of the textiles after the adhesion testing.

In the recent literature, laboratory scale adhesion testing experiments, or in technical wording, "colour fastness" were conducted by (i) light exposure (**Hinsch and Robinson 2018**), (ii) washing and flexibility (**Monzavi et al. 2017**), and (iii) rubbing (**Zou et al. 2018**). In this context, we wished to contribute to this topic by bridging the gap between adhesion phenomena and photocatalysis. In the course of the investigation of adhesion of TiO_2 to the textiles by an ultrasonic test ("ultrasonic colour fastness"), we surprisingly discovered that the ultrasonic waves increased the photocatalytic activity of TiO_2 NPs. This good example of serendipity has encouraged us to deepen the study of the ultrasonic effect on the photocatalytic properties of TiO_2-immobilized textiles.

In this paper, we describe the use of a cotton fabric that has been coated with TiO_2 nanoparticles for the photocatalyzed destruction of Rhodamine 6G (Rh6G) taken as model organic dye as well as the frequently investigated Methylene Blue. The rationale for choosing these model compounds for testing textile photocatalyst is the following: Rhodamine 6G is a product with well-known toxicity. Its LD50 lethal dose is 89.5 mg/kg for rats. Rh6G is specifically used as a tracer dye in water to determine volumes, flow rates and directions of flow and transport. Methylene Blue is most often used as a disinfectant and can be found in natural waters through medical discharges. The presence of these two compounds in the aquatic environment can be harmful for the environment (**Budavari et al. 1989; Program 1989; Djaneye-Boundjou et al. 2001; George and Kishen 2007**).

The TiO_2 NPs were prepared *in situ* in the presence of cotton fabric and activated by a hydrothermal treatment. The resulting hybrid textile has shown good photocatalytic activity for the degradation of Remazol Brilliant Blue R (**Abid et al. 2016**). This method of preparation of such specific fabrics is reliable and easy to produce. Although, much progress has been made in the production of TiO_2-modified smart textiles, the examination of the photocatalytic properties of the final product after adhesion test of TiO_2 remains sparse despite the technological interest of this kind of investigation to the textile industry, hence the motivation for this in-depth study.

Nanostructured cotton samples were characterized by several techniques (SEM, XPS, UV-Vis and FTIR spectroscopy, GSDR and LIL). The final fabric/TiO_2 was used to degrade Rhodamine 6G. The photodegradation of the dye molecules in fabric/TiO_2-containing solutions exposed to a sun simulator was monitored by the colour change, observed by naked eye and UV/Vis absorption spectroscopy.

Experimental

Chemicals

Chemical reagents were provided by Sigma Aldrich were of analytical grade and used without further purification: $Ti(OBu)_4$, glacial acetic acid, Rhodamine 6G (~95%), tert-butanol 99.7%. Cotton fabrics were common gauze bandages with more than 99% of cellulose (purchased from Mega, Médicale Gaze S.A.).

Preparation of cotton fabrics/TiO_2

The cotton fabrics/TiO_2 samples were prepared as previously reported **(Abid et al. 2016**). It is a non-hydrolytic sol-gel process followed by a mild hydrothermal treatment at a temperature below 140 °C. We used samples prepared at different temperatures (50, 110, 120 and 140 °C).

Sonication of cotton fabrics

The samples were placed in vials containing deionized water and subjected to ultrasonication in a sonocleaner (Bandelin, Sonorex Digitec model; 860 W, 35kHz) for 5, 15 or 30 min. After sonication, they were washed with water, and dried for further studies.

Characterization

Scanning electron microscopy images were recorded using a Field Emission Scanning Electron Microscope (FE-SEM) ZEISS SUPRA40, previously described (**Abid et al. 2016**).

X-ray photoelectron spectroscopy (XPS) measurements were recorded using a K Alpha system (Thermo Fisher Scientific) fitted with Al X-ray source ($h\nu$=1486.6 eV; spot size=400 µm) and an electron flood gun. Surface composition was determined using the manufacturer's sensitivity factors.

FTIR spectra were acquired using a Bruker Tensor 27 IR spectrometer in the range of 400-4000 cm^{-1} spectral region. Samples were first washed 3 times with distilled water and dried before analysis.

Ground state diffuse reflectance (GSDR) absorption spectra were recorded using an OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given elsewhere (**Vieira Ferreira and Ferreira Machado 2007; Errokh et al. 2016**).

The set-up for the laser induced luminescence (LIL) was described in the literature (**Errokh et al. 2016**). Time-resolved emission spectra were performed in the nanosecond to second time range with a N_2 laser (excitation wavelength=337 nm, PTI model 2000, ca. 600 ps FWHM, about 1 mJ per pulse). Emission spectra were obtained at 77 K, due to the fact that, at the room temperature, luminescence intensity is negligible for the anatase form of TiO_2.

Photocatalytic measurements

The irradiation tests were carried out using UVACUBE400 photoreactor, producing a simulated sunlight; this device was used to test the photocatalytic activity of the cotton fabrics/TiO_2 samples. All measurements were performed with 30 mg (per step) of fabric/TiO_2 in 6 ml of a Rh6G solution (5 mg/L) stored in the dark for 45 min to reach the adsorption equilibrium. The absorbance of the Rh6G solution was monitored using a Varian Cary 50 Bio UV-visible spectrophotometer controlled by the CaryWinUV software.

Results and discussion

The sequential steps of the work are presented in Fig. 1. In the first step of the preparation of cotton-TiO_2, woven cotton samples were immersed in a solution of $Ti(OBu)_4$ in tert-butanol for 12 hours at room temperature. Then, after drying, the cotton fabrics were subjected to mild hydrothermal treatment for 3 hours at indicated temperature to crystallize the TiO_2 layer generated on the surface of the cotton fibers (**Abid et al. 2016**). These samples have been tested to determine optimal conditions for high performance photocatalytic activity.

Cotton-TiO_2 samples were then sonicated at room temperature (Fig. 1(a)). 30 mg of each sample was placed in a beaker containing 10 ml of distilled water and sonicated for 30 minutes.

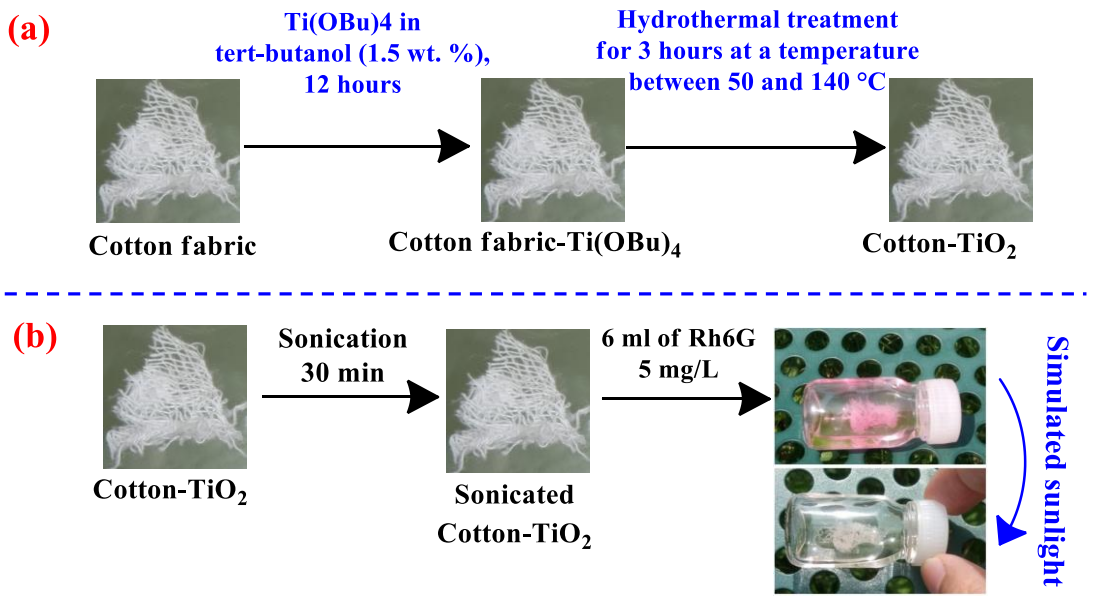


Fig. 1 Illustration of the different steps followed to : (a) prepare different cotton-TiO_2 NPs samples and (b) sonication and photodegradation of Rh6G.

Scanning electron microscopy (SEM)

The SEM images of the different cotton samples are shown in Fig. 2. The morphology of cotton cellulose fibres prior to hydrothermal treatment is shown in Fig. 2(a). *In situ* synthesis of TiO_2 nanoparticles the latter for a very thin layer that is topping the cotton fibres. The mean size of the TiO_2 NPs is less than 20 nm for the hydrothermal treatment at 120 °C.

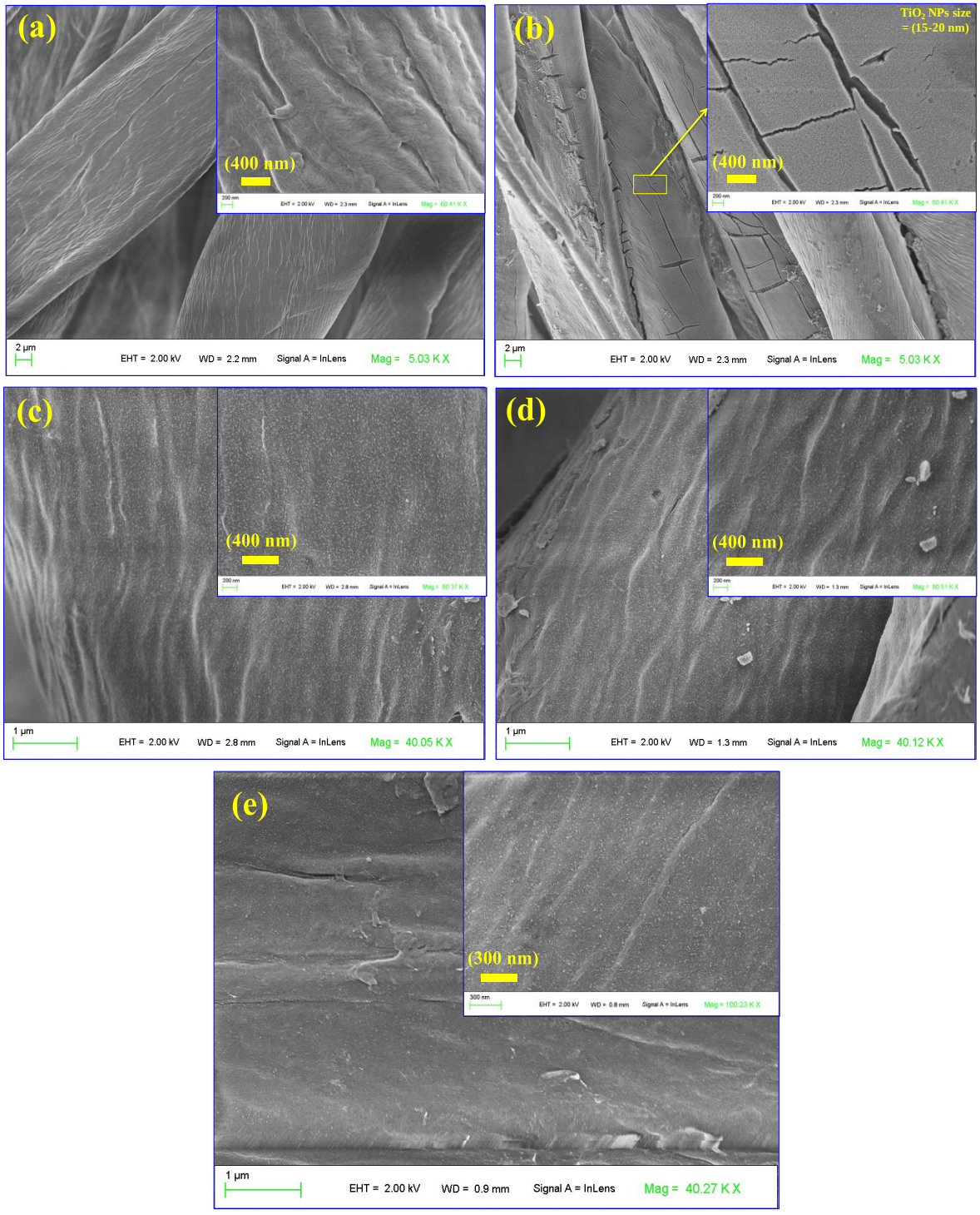


Fig. 2 SEM images: (a) top view of pristine cotton substrate; (b) cotton fabric/TiO_2-120 °C; (c) sonicated cotton fabric/TiO_2-120 °C/5 min; (d) sonicated cotton fabric/TiO_2-120 °C/30 min and (e) cotton fabric/TiO_2-120 °C after 4 hours and 30 min exposure to simulated sunlight

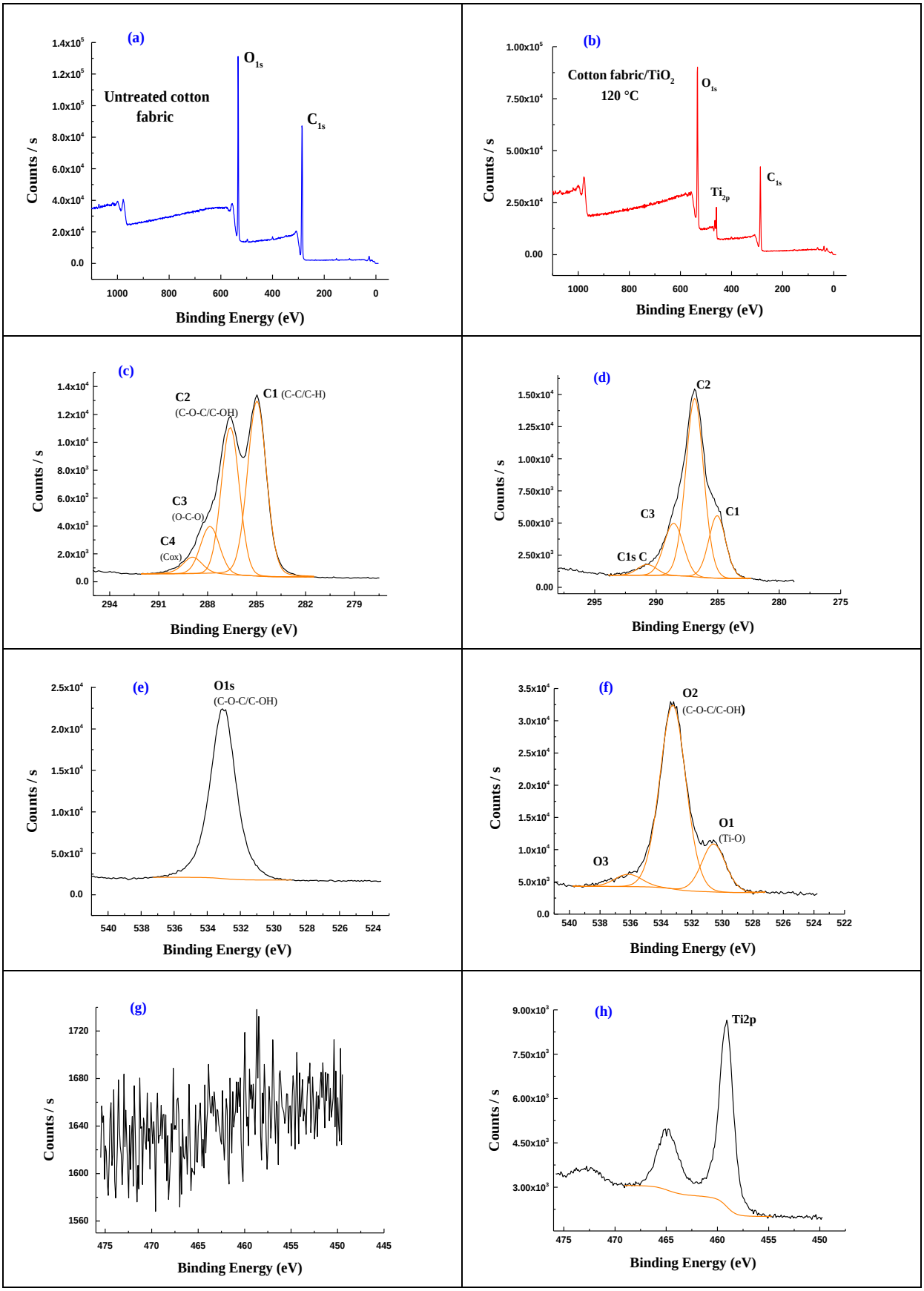
Fabric/TiO_2 samples were sonicated for 5, 15 and 30 minutes to test the adhesion between the TiO_2 NPs layer and the woven cotton surface. Fig. 2(c) shows Fabric/TiO_2-120 °C after 5 minutes of sonication; one can note that the TiO_2 NPs layer withstands sonication even after 30 minutes of sonication. Another important observation concerns the

homogeneous spreading of TiO_2 NPs over the entire cotton fabrics (Figs. 2(c-d)) compared to the surface shown in Fig. 2(b). To study the robustness of the catalytic property of the TiO_2-containing fabric relatively to the irradiation of the simulated sunlight, a UVACUBE400 reactor was used. Indeed, the exposure of fabric/TiO_2 for one hour in the sun simulator corresponds to about 9 days and 2 hours of exposure to the sun. The fabric/TiO_2 sample is introduced in a tube and stays under insolation for 4 hours and 30 min in the photoreactor, corresponding to 40 days and 9 hours of day light exposure. SEM image shown in Fig. 2(e) confirms that the simulated sunlight treated surface remains identical to the sonicated one (image (d)).

X-ray photoelectron spectroscopy (XPS)

Fig. 3 displays XPS spectra of untreated cotton (Fig. 3 (a, c, e, g)) and TiO_2 loaded cotton fabric-120 °C (b, d, f, h). Survey regions are displayed in Fig. 3 (a (untreated cotton) and b (Fabric/TiO_2-120 °C)); and the main peaks are C1s (285 eV), Ti2p (459 eV) and O1s (532 eV). The untreated cotton does not contain TiO_2 NPs, which was confirmed by the shape of Ti2p line obtained in Fig. 3(g), whereas fabric/TiO_2-120 °C spectrum exhibits a peak at 459 eV corresponding to Ti2p (Fig. 3(h)), which proves that the immobilization step of TiO_2 NPs on cotton samples was successfully accomplished. The C1s region presented in Fig. 3(c, d) was fitted with four components centred at 285.0, 286.6, 288.3 and 289.5 eV, assigned to: C-C/C-H bonds derived from the hydrocarbon contamination or treatment of cotton fabrics (sizing); C-O-C/C-OH, O-C-O bonds corresponding to the hemi-acetal group characteristic of cellulose; and finally, an oxidation peak which corresponds to an ester or an adsorbed carbonate. Since a cellulose unit has only one hemiacetal carbon atom, we will choose this atom as a marker element for cellulose in the following (**Belgacem et al. 1995; Attia et al. 2013**).

The O1s XPS region presented in Fig. 3 (e) reveals an asymmetric peak at 533.0 eV attributed to C-O bonds in cellulose and other organic compounds. While for fabric/TiO_2-120 °C, there is an additional contribution centred at 530.5 eV, which is characteristic of metallic oxides and herein assigned to Ti-O bond (**Atashbar et al. 1998**).



212 **Fig. 3** XPS spectra of untreated cotton fabric (a, c, e, g) and cotton fabric/TiO_2-120 °C (b, d, f, h)

XPS spectra were recorded for fabrics/TiO_2-(50, 110 and 140 °C). Table 1 shows the chemical composition of the untreated and TiO_2 loaded cotton fabrics. The cotton fabric used is contaminated even if it is a sterile sample. In fact, hydrocarbons contribute 33.2% to the composition of untreated cotton (regardless of hydrogen). Once TiO_2 has been deposited, this contribution is substantially reduced. We note also that the atomic percentage of TiO_2 is higher for the refluxed cotton fabric sample at 120 °C; this variation may be due to the difference in reflux temperatures.

Table 1 Surface chemical composition of untreated and TiO_2 loaded woven cotton fabrics.

Samples	C1 (C-C/C-H)	C2 (C-O-C/C-OH)	C3 (O-C-O)	C4 (CO_x)	O1 (TiO_2)	O2 (org)	Ti
Untreated cotton fabric	33.20	25.90	8.86	3.51	-	28.60	-
Fabric/TiO_2-50 °C	11.23	29.75	12.74	2.52	3.72	38.11	1.92
Fabric/TiO_2-110 °C	14.64	30.16	10.06	2.13	7.56	33.10	2.45
Fabric/TiO_2-120 °C	11.01	32.89	10.20	2.10	7.42	12.30	3.14
Fabric/TiO_2-140 °C	18.75	25.34	9.54	3.11	6.24	34.10	3.01

In order to study the effect of the adhesion test (sonication) on the fabric/TiO_2 as well as the effect of the exposure to simulated sunlight on the stability of the photocatalytic activity of TiO_2 NPs, 4 samples of 30 mg of cotton fabric/TiO_2-120 °C were taken for post-treatment under ultrasonic waves for 5, 15 and 30 min, respectively; and the 4th sample was placed in the photoreactor for an insolation of 4h30. These samples were then analysed in XPS, and the ratio Ti/C3 (Fig. 4) was compared, Ti being the marker element of titanium oxide and C3 that of cellulose. One can remark that the atomic percentage of Ti increases from a non-post-treated fabric/TiO_2-120 °C to a sonicated sample and the sonication time. This may be due to the fact that sonication leaves the distribution of TiO_2 NPs more homogeneous on the surface of the cotton fibres, improving the screening of the fabric. The ratio Ti/C3 for the insolated sample for 4 hours 30 min still reveals a high percentage of Ti, confirming that titanium oxide remains on the fabric surface despite the long treatment in the photoreactor.

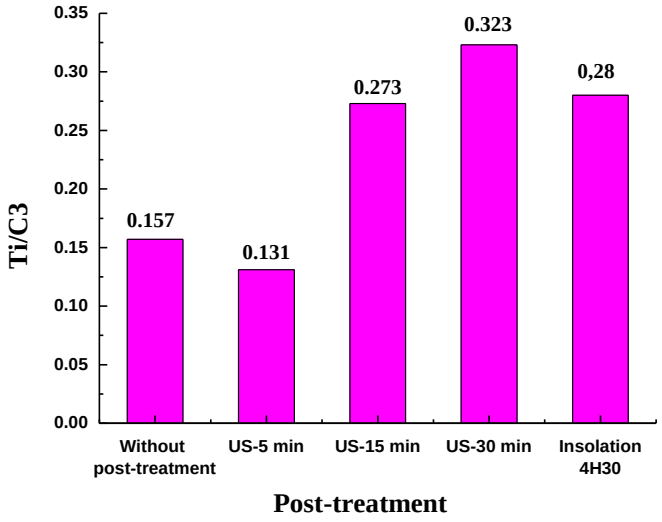


Fig. 4 Atomic ratios (Ti/C3) of samples untreated or treated (sonication and insolation) undergone by a fabric/TiO_2-120 °C sample

Effect of fabric/TiO_2 treatment on the catalysed photodegradation of Rhodamine 6G

Stability of the dye and degradation time

Prior to any photocatalytic test, a 5 mg/L aqueous solution of the model dye Rhodamine 6G (Rh6G) was exposed to simulated sunlight in the absence of the fabric. Similarly, spectra of Rh6G solutions exposed to the photoreactor in the presence of fabric/TiO_2-120 °C were recorded to check the stability of the dye before and after contact with the photocatalytic textile. Fig. 5 shows the UV-vis spectra for this assay as well as the chemical formula of the Rh6G dye. It should be noted that the aqueous solution of Rh6G gives a peak at 525 nm and after exposure to the simulated sunlight, the absorbance remains the same, that is to say that the Rh6G was not degraded under irradiation at photoreactor for 120 minutes. This indicates that this dye is stable and can be used for testing the photocatalytic activity of the textile catalytic samples as it does not give any false positive result.

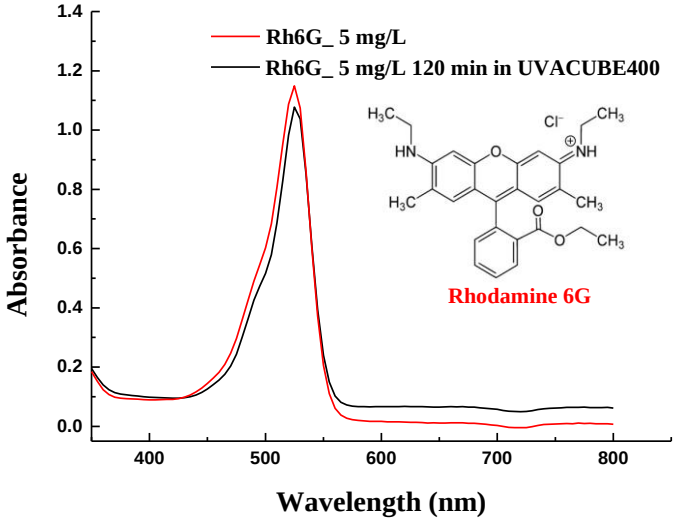


Fig. 5 UV-Vis absorption spectra of Rh6G before and after irradiation in the UVACUBE400 photoreactor

To optimize the exposure time of the dye/textile mixture to light, several tests at different time intervals (20, 40, 60 and 120 min) were performed, considering the start time t_0=45 min prior in the obscurity. The different UV-vis spectra compared in Fig.6, which show a progressive decrease in the maximum intensity of the initial Rh6G solution in the presence of fabric/TiO_2-120 °C from the beginning up to 2 hours of the insolation exposure. After 120 min exposure of the Rh6G dye to light, the aqueous solution becomes colourless, which is here conferred to the activity of the photocatalytic textile, proving the photocatalytic activity of TiO_2 nanoparticles immobilized on the cotton fibres. However, the photocatalytic activity decreases after several operations. This may be associated to the presence of aggregating by-products on the surface of the photocatalyst (**Hamden et al. 2014**). On the one hand, Rh6G is stable after long exposure to simulated sunlight, and on the other hand the textile catalyst is active and induces bleaching of the dye.

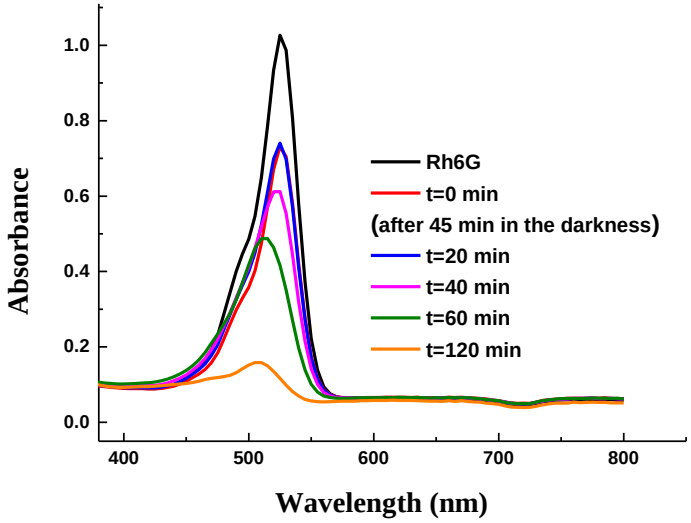


Fig. 6 UV-Vis absorption spectra of Rh6G with and without fabric/TiO2-120 °C at different time intervals under UV irradiation

Dual effects of hydrothermal and post-sonication treatments on the catalytic fabrics

The treated fabric/TiO_2 hybrid nanocomposites were refluxed to 50, 110, 120 and 140 °C then introduced to Rh6G aqueous solution before exposure to simulated sunlight. After sunlight irradiation for 120 minutes, all vials turned colourless which denotes the effective photocatalytic activity of the immobilized TiO_2 NPs. The sharp decrease in absorbance after exposure of the dye/textile mixtures to light in Fig. 7(a) emphasizes the successful photocatalytic degradation of Rh6G in the presence of the refluxed fabrics after being UV irradiated for 120 minutes.

Furthermore, the hydrothermal treatment carried out at different temperatures undergone by the fabric/TiO_2 influences the catalytic power of TiO_2 NPs. It is noted that the optimum temperature for photodegradation of Rh6G is 120 °C (Fig. 7(a)). At higher temperature; namely 140 °C, we have a higher absorbance value than that obtained for the fabric prepared at 120 °C indicating a decrease in the photocatalytic activity at higher temperatures than 120 °C as previously reported (**Abid et al. 2016**).

An approach by means of ultrasonication (US) has been endeavoured with fabric/TiO_2 to test the adhesion of TiO_2 to the cotton fabric. Three vials; each containing (30 mg of treated fabric/TiO_2) were ultrasonicated for 5, 15 and 30 min. Then, the samples were washed 3 times with distilled water. This was followed by placing 6 ml of the prepared Rh6G solution in each

vial containing the ultrasonicated treated fabrics and subjecting them to simulated sunlight exposure for 120 minutes. The effect of post-sonication is shown in Fig.7(a) (red bars). As one can observe, there is a significant decrease in absorbance compared to non-ultrasound samples. This means that despite partial removal of the catalytic nanoparticles, the fabrics retain photocatalytic activity. Surprisingly, the decrease in the spectral peak intensity of the dye is systematically lower for post-sonicated hydrothermally treated fabrics, up to 120 °C. This difference is significant and is not contained within the error bars, therefore testifying a true synergetic effect of ultrasonication on the fabric. There is an exception for the TiO_2-modified fabric that has been treated hydrothermally at 140 °C: we noted slight increase of absorbance, mostly due to slight adhesion loss of TiO_2 nanoparticles. Indeed, XPS analysis of cotton-TiO_2 samples reported in Table 1 shows that annealed sample at 140 °C has a Ti at.% of 3.01% , slightly lower compared to 3.14% for 120 °C annealing temperature. Sonication does not improve the photocatalytic character of the fabric annealed at 140 °C; for this reason we further examined the performances of the fabric annealed at 120 °C (see Fig. 7b).

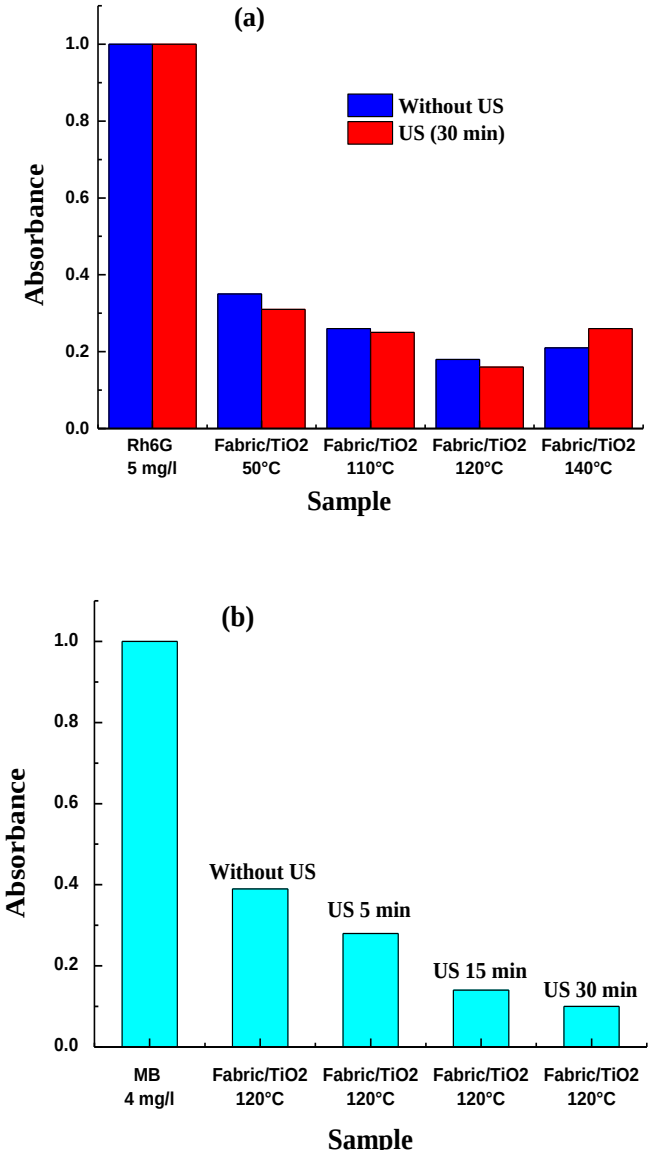


Fig. 7 (a) UV-Vis absorption spectra of Rh6G after photocatalytic degradation in the presence of non-sonicated and sonicated fabric/TiO_2 refluxed at (50, 110, 120 and 140 °C) subjected to UV irradiation. (b) Photodegradation spectrum of methylene blue with fabric/TiO_2-120 °C with and without sonication

To confirm that sonication increases the photocatalytic effect of TiO_2 NPs, we repeated a similar experiment with a fabric that has been hydrothermally treated at 120 °C. Three samples of this fabric were post-sonicated for 5, 15 and 30 min and then used to catalyse the photodegradation of Methylene Blue, MB (Fig.7(b)). It is clear that the fabric continues to act as a true photocatalyst after sonication since the maximum absorbance of the MB decreases by 60% compared to the pure MB solution (4 mg/L) after a short sonication period

(5 minutes). On the other hand, after a sonication of 30 minutes, one reaches to attain 90% of degradation of MB.

The results displayed in Fig. 7 demonstrate the important improvement of the photocatalytic performances of TiO_2 loaded cotton fabrics. This unexpected result, accounts for the morphology displayed in the SEM images, which show that after sonication the surface of the cotton becomes more homogeneous. Possibly, with an even distribution of the cotton fabric, a larger specific surface was achieved by the TiO_2 NPs that remained on the textile.

The adhesion between the cotton fabric and TiO_2 after sonication has been studied by FT-IR spectroscopy in transmission mode. Hence, the treated fabrics were washed 3 times with distilled water and dried before analysed by FTIRS. Fig. 8 illustrates the infrared spectra of treated fabric/TiO_2, showing no changes in the wave numbers of the characteristic peaks of the three treated samples after 5, 15 and 30 minutes of sonication. Cellulosic chains are characterized by different bands, a broad one corresponding to the O-H stretching located at 3320 cm^{-1}, the C-H stretching at 2886 cm^{-1} with the corresponding C-H bending at 1430 cm^{-1}, -O-H bending at 1630 and at 1418 cm^{-1} stretching vibrations. In addition, the peak at 1031 cm^{-1} refers to symmetric and asymmetric stretching C-O-C bonds. The peak that appears at 690 cm^{-1} is assigned to Ti-O-O bond and accounts for the presence of TiO_2 after sonication. These results show that despite this strong sonication test, the characteristic peak of TiO_2 NPs is always present.

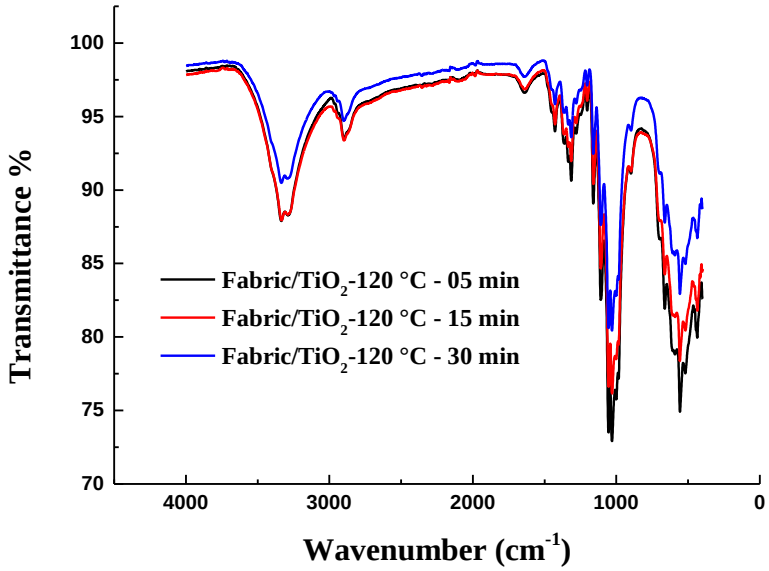


Fig. 8 FTIR spectra of treated Fabric/TiO_2-120 °C ultrasonicated during 5, 15 and 30 minutes

Ground-state diffuse reflectance

The ground-state diffuse reflectance spectra of fabric/TiO_2 before and after ultrasonic vibration are shown in Fig. 9. The UV absorption band at about 310 nm corresponding to TiO_2, already studied and reported in a previous work (**Abid et al. 2016**), proves the existence of TiO_2 NPs on cotton fibres.

The presence of the same peak at about 312 nm after sonication shows that this test does not detach the TiO_2 NPs from the cotton substrate, i.e. the bond is strong between the TiO_2 NPs and cotton fibres.

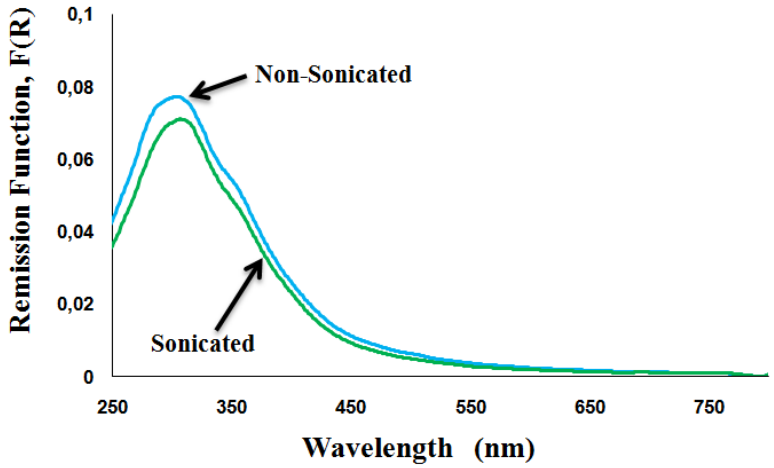


Fig. 9 Ground State Diffuse Reflectance (GSDR) spectra of Fabric/TiO_2 sample before and after sonication

However, a small amount of TiO_2 is detached from the substrate, as the decrease of the remission function value for the sonicated sample clearly shows.

Laser induced luminescence

The laser induced luminescence spectra (λ_{exc}=337 nm, ~1.3 mJ per excitation pulse), at 77 K, for the fabric/TiO_2 samples are illustrated in Fig. 10(a). The initial curve was obtained after laser pulse, and the following curves were obtained with the step of 1000 ns. The gate width was 10 ms. The laser induced emission spectra of non-sonicated fabric/TiO_2 are displayed with maxima at 533 nm. The maximum emission of non-sonicated fabric/TiO_2, was obtained with a maximum of about 533 nm (Fig. 10(a)) and a luminescence intensity of about 150000 (a.u.). These spectra reflect a simultaneous emission of cotton and TiO_2 with a greater contribution of the latter. After ultrasonic treatment with fabric/TiO_2-120 °C (Fig. 10(b)), the luminescence intensity increases to about 230000 (a.u.). This large difference between the two spectra is certainly due to the effect of sonication on the distribution and the organization of TiO_2 NPs immobilized on the fabric. Only the better attached TiO_2 NPs remain on the surface and possibly the number of surface defects decreases with sonication, meaning that the number of traps for the excited TiO_2 to be deactivated by a non-radiative pathway also decreases. Therefore, the luminescence intensity of TiO_2 increases for the sonicated sample and also the half-life is about 1.5 μs, while the non-sonicated sample exhibits a shorter half-life, at least in the initial times of its decay. These data also support the interpretation that the remaining TiO_2 NPs (after sonication) contain less defects (traps), therefore larger intensities for irs luminescence and larger lifetimes for the TiO_2 NPs are observed.

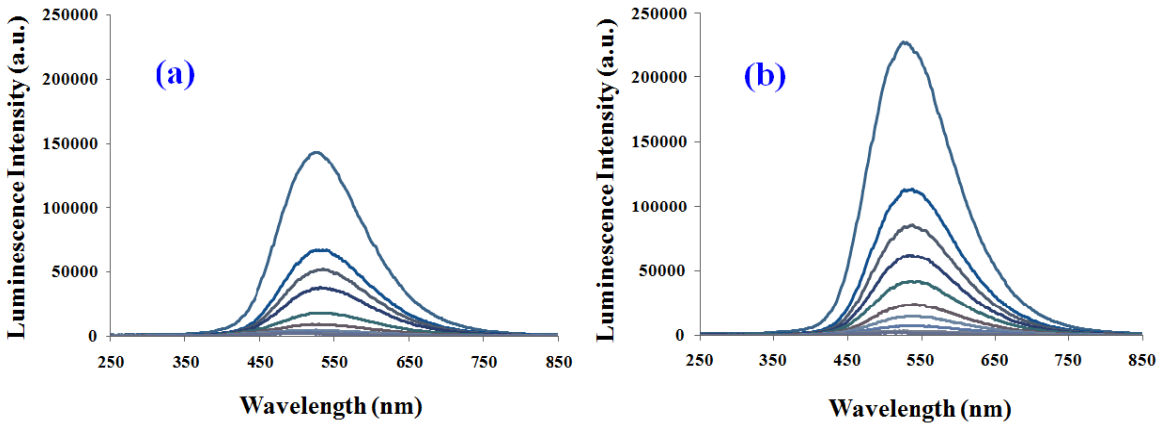


Fig. 10 Laser induced luminescence spectra, obtained at 77 K, of Fabric/TiO_2-120 °C samples (a) before sonication and (b) after sonication. The excitation wavelength was 337 nm and the step was 1 μs in both cases. The used gate width was 10 ms

Conclusion

Woven cotton textile samples loaded with TiO_2 NPs were hydrothermally treated at temperatures ranging from 50 °C to 140 °C. The presence of TiO_2 on the samples was verified by several characterization techniques and the photocatalytic activity was found optimized for a hydrothermal treatment at 120 °C, as judged from the results obtained with a model dye Rhodamine 6G (Rh6G). In our quest of photocatalytic pigment fastness, we subjected the samples to ultrasonication to check their ability to remain attached to the surface. In a serendipitous way, we found out that ultrasonication boosted the photocatalytic effect despite a slight partial removal of TiO_2 nanoparticles. The study was repeated with Methylene Blue dye, and a similar effect was observed as the photocatalyzed degradation of MB led to a loss of 90% after 30 min of ultrasonication of the fabric primarily hydrothermally treated at 120 °C. Compared to un-sonicated fabric the photocatalyzed degradation using a sonicated catalytic fabric is 4 times better as the non-sonicated fabric degraded MB but left 40% of the dye.

This work conclusively shows that ultrasonication clearly boosts up the photocatalytic activity of TiO_2, and the process could be extended to other types of nanocatalysts such as mixed oxides or noble metal loaded TiO_2. The process is simple and could be generalized for pilot testing.

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